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(54) INJECTION MOLDING FOAMED MATERIALS

GESCHÄUMTE SPRITZGUSS-MATERIALIEN

MATERIAUX EN MOUSSE PAR MOULAGE PAR INJECTION

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Description

Introduction

[0001] This invention relates generally to foamed materials, preferably foamed plastic materials, and to techniques for making and using such materials, and, more particularly, to the use of supercritical fluids for producing supermicrocellular foamed materials which can achieve a relatively wide range of material densities and a large number of extremely small voids or cells per unit volume therein.

Background of the Invention

[0002] Techniques for making conventional foamed materials, such as foamed polymer plastic materials, have been well known for many years. Standard techniques for such purpose normally use chemical or physical blowing agents. The use of chemical agents is described, for example, by Lacallade in the text, "Plastics Engineering," Vol. 32, June 1976 which discusses various chemical blowing agents, which agents are generally low molecular weight organic compounds which decompose at a critical temperature and release a gas (or gases) such as nitrogen, carbon dioxide, or carbon monoxide. Techniques using physical agents include the introduction of a gas as a component of a polymer charge or the introduction of gases under pressure into molten polymer. Injection of a gas into a flowing stream of molten plastic is described, for example, in U.S. Patent No. 3,796,779 issued to Greenberg on March 12, 1976. Such earlier used and standard foaming processes produce voids or cells within the plastic materials which are relatively large, e.g., on the order of 100 μm, or greater, as well as relatively wide ranges of void fraction percentages, e.g., from 20%-90% of the parent material. The number of voids per unit volume is relatively low and often there is a generally non-uniform distribution of such cells throughout the foamed material. Such materials tend to have relatively low mechanical strengths and toughness and there is an inability to control the dielectric constant thereof.

[0003] In order to improve the mechanical properties of such standard cellular foamed materials, a microcellular process was developed for manufacturing foamed plastics having greater cell densities and smaller cell sizes. Such a process is described, for example, in U. S. Patent No. 4,473,665 issued on September 25, 1984 to J. E. Martini-Vredensky et al. The improved technique provides for presaturating the plastic material to be processed with a uniform concentration of a gas under pressure and the provision of a sudden induction of thermodynamic instability in order to nucleate a large number of cells. For example, the material is presaturated with the gas and maintained under pressure at a glass transition temperature. The material is suddenly exposed to a low pressure to nucleate cells and promote cell growth to a desired size, depending on the desired final density, thereby producing a foamed material having microcellular voids, or cells, therein. The material is then quickly further cooled, or quenched, to maintain the microcellular structure.

[0004] Such a technique tends to increase the cell density, i.e., the number of cells per unit volume of the parent material, and to produce much smaller cell sizes than those in standard cellular structures. The microcellular process described tends to provide cell sizes that are generally smaller than the critical sizes that preexist in polymers so that the densities and the composition of the materials involved can be controlled without sacrificing the desired cell characteristics thereof, while at the same time enhancing the mechanical properties in some polymers, such as the mechanical strength and toughness of the polymer. The resulting microcellular foamed materials that are produced, using various thermoplastics and thermosetting plastics, tend to have average cell sizes on the order of 10 μm, with void fractions of up to 50% of the total volume and maximum cell densities of about one billion (10^9) voids per cubic centimeter of the parent material.

[0005] Further work in producing microcellular foamed plastic material is described in U.S. Patent No. 4,761,256 issued on August 2, 1988 to Hardenbrook et al. As set forth therein, a web of plastic material is impregnated with an inert gas and the gas is diffused out of the web in a controlled manner. The web is reheated at a foaming station to induce foaming, the temperature and duration of the foaming process being controlled prior to the generation of the web to produce the desired characteristics. The process is designed to provide for production of foamed plastic web materials in a continuous manner. The cell sizes in the foamed material appear to lie within a range from 2 to 9 μm in diameter.

[0006] It is desirable to obtain improved foamed materials which will provide even smaller cell sizes, e.g., as small as 1.0 μm or less, and much higher cell densities as high as several trillions of voids per cubic centimeter, i.e., on the order of 10^{15}, or so, voids per cubic centimeter of the parent material, for example. Such materials should also have a capability of providing a wide range of void fraction percentages from very high void fractions (low material densities) up to 90%, or more, to very low void fractions (high material densities) down to 20%, or less.

[0007] Further, it is desirable to be able to produce microcellular plastics at or near ambient temperature, so as to eliminate the need to heat the plastic during the process thereby simplifying the manufacturing process. Moreover, it is further desirable to increase the speed at which a fluid is dissolved in a polymer so that the overall time of the foaming process can be significantly reduced so as to increase the rate of production of the foamed material.

[0008] No processes used or proposed for use to date have been able to provide foamed materials having

such extremely small cell sizes, such extremely high cell densities and such a wide range of material densities that provide improved material characteristics. Nor have techniques been proposed to obtain such materials at ambient temperature and at increased production rates.

Brief Summary of the Invention

[0009] In accordance with the invention, as defined in claim 1 hereinbelow, supermicrocellular foamed materials are formed by using supercritical fluids, i.e., gases in their supercritical state, which supercritical fluids are supplied to the materials to be foamed. The supercritical fluid is used as the foaming agent in a parent material, preferably, for example, in a polymer plastic material. A relatively high density supercritical fluid made at a relatively low temperature and a relatively high pressure is used to saturate the polymer without the need to raise the saturation temperature of the process to the melting point of the polymer.

[0010] While the mechanism for achieving saturation is not fully understood in detail, it is believed that the supercritical fluid (as a solute) is initially dissolved in the polymer material (as a solvent) until the concentration percentage of supercritical fluid in the polymer reaches a reasonable level, e.g., perhaps about 10% to 20%. At some percentage level then, it is believed that supercritical fluid then tends to act as a solvent and the polymer tends to act as a solute. However, whether the supercritical fluid and polymer act as solvents or solutes during the process, at some time following the introduction of supercritical fluid into the polymer, an effectively saturated solution of the fluid and the polymer is produced. Although the aforesaid description is believed to be a reasonable theoretical explanation of what occurs during the process involved, the invention is not be construed as requiring that such specific process necessarily occurs in the manner so described.

[0011] When the fluid/polymer solution contains a sufficient amount of supercritical fluid therein at a suitably selected temperature and pressure, the temperature and/or pressure of the fluid/polymer system is rapidly changed to induce a thermodynamic instability and a foamed polymer is produced. The resulting foamed material can achieve a cell density of several hundred trillions of voids per cubic centimeter and average void or cell sizes of less than 1.0 μm, in some cases less than 0.5 μm. Moreover, in accordance with the invention, the foaming of such materials can in some cases be achieved at ambient (room) temperature conditions.

Description of the Invention

[0012] The invention can be described in more detail with the help of the following drawings wherein

FIGS. 1 and 1A depict graphs of the pressure vs. specific volume relationship showing the region in which a supercritical state is achieved for carbon dioxide;

FIG. 1B depicts a graph of the pressure vs. temperature relationship showing the region in which a supercritical state is achieved for carbon dioxide;

FIG. 2 depicts a chart of critical temperatures and critical pressures required for placing various materials in their supercritical fluid states;

FIG. 3 depicts a diagrammatic view of a system for forming supermicrocellular foamed materials;

FIGS. 4 and 5 depict graphs of pressure vs. volume relationships helpful in understanding an exemplary method of the invention for an ideal and for an actual operation of the system of FIG. 3 when using carbon dioxide;

FIGS. 6, 7, 8, 9, 10, and 11 depict microphotographs showing typical cross-section views of the cells produced in various supermicrocellular foamed materials ;

FIG. 12 depicts bar graphs of the average cell sizes produced for various supermicrocellular foamed polymer plastic materials formed under substantially the same exemplary conditions;

FIG. 13 depicts bar graphs of the average cell densities produced for the various supermicrocellular foamed polymer plastic materials shown in FIG. 12 formed under substantially the same exemplary conditions; ; and

FIG. 18 depicts an injection molding system in accordance with the invention in which the time required for saturation of a material by a supercritical fluid is greatly reduced from that normally required for microcellular foaming.

[0013] A supercritical fluid can be defined as a material which is maintained at a temperature which exceeds a critical temperature and at a pressure which exceeds a critical pressure so as to place the material in a supercritical fluid state. In such state, the supercritical fluid has properties which cause it to act, in effect, as both a gas and a liquid. Thus, in the supercritical state, such a fluid has the solvent characteristics of a liquid, but the surface tension thereof is substantially less than that of a liquid so that the fluid can diffuse much more readily into a solute material, as in the nature of a gas.

[0014] For example, it is known that carbon dioxide (CO_2) can be placed in a supercritical state when its temperature exceeds 31°C and its pressure exceeds 7.5 MPa (1100 psi). FIGS. 1 and 1A, for example, depict curves 10 and 12 of pressure vs. specific volume (FIG. 1) and temperature vs. specific entropy (FIG. 1A) for carbon dioxide. When the pressure is above 7.5 MPa (1100 psi) and the temperature is above 31°C (curve 10A) exemplified by the shaded region 11 of FIG. 1, and when the temperature is above about 31° C and the pressure is above 7.5MPa (1100 psi) (curve 12A) exemplified by the shaded region 13 of FIG. 1A, carbon dioxide is provided in its supercritical state. As depicted another way,

FIG. 1B shows the pressure vs. temperature relationship for CO_2 in which such critical pressure 7.5MPa (1100 psi) and critical temperature (31° C) are depicted so as to define the supercritical state by the shaded region 14.

[0015] The chart of FIG. 2 depicts the critical temperatures and pressures for various known exemplary materials, above which values such materials are placed in their supercritical fluid states.

[0016] FIG. 3 shows a diagrammatic view of an exemplary system for use in forming supercritical foamed materials. As can be seen therein, a source of carbon dioxide in a non-critical state is provided from a pressurized CO_2 cylinder 20 in which CO_2 is maintained at a pressure and temperature below the above discussed critical values. The CO_2 therein is supplied through conduit 21 via a high-pressure valve 22 to a high pressure chamber 23.

[0017] The temperature of the chamber can be controlled, for example, by placing the chamber in a temperature controlled enclosure 24. A material 25, such as a polymer plastic material, is placed within chamber 23. The temperature of the chamber is controlled to be set at a selected initial temperature level.

[0018] In order to understand the process of providing a supercritical fluid, such as CO_2 in its supercritical state, to chamber 23 for use in producing a foamed material, it is helpful to consider the pressure-volume relationships shown in FIGS. 4 and 5 which depict such relationships both ideally (FIG. 4) and in an actual experimental case (FIGS. 5) when CO_2 is used in its supercritical fluid state with a soft polyvinyl chloride polymer plastic.

[0019] In accordance with a specific exemplary process for providing a supercritical CO_2 fluid, the temperature of chamber 23 is initially set at 25° C, via a suitable temperature control of enclosure 24 using control techniques as would be well-known to those in the art. A CO_2 gas is maintained in cylinder 20 at a pressure of 850 psi (5.8 MPa), for example, and high pressure valve 22 is opened to supply CO_2 gas at such pressure to chamber 23 via conduit 21. Valve 22 is closed (point A of FIGS. 4 and 5) so that initial conditions of a temperature of 25° C and a pressure of 5.8 MPa (850 psi) are established in chamber 24.

[0020] The temperature of chamber 24 is then reduced to 0° C at which point the pressure drops to 3.5MPa (515 psi) (point B of FIGS. 4 and 5). The specific volume is reduced and the high pressure valve 22 is then opened (point B of FIGS. 4 and 5), so that the pressure in chamber 23 again rises to the 5.8 MPa (850 psi) level of the CO_2 cylinder (point C of FIGS. 4 and 5). The temperature of the chamber is then again controlled so as to increase from 0° C to a much higher temperature, selected in this exemplary case as 43° C. The pressure rises from 5.8 MPa (850 psi) to a much higher value shown theoretically in the ideal case as 41MPa (6000 psi) (point D of FIG. 4). In a practical case, the pressure must be controlled so as not to exceed the limits imposed by the chamber 23. In a practical case, the high pressure value, for example, is increased to 20.5MPa, (3000 psi) (point D of FIG.5).

[0021] At point D, the CO_2 is in a supercritical state and acts as a supercritical fluid. At such point, the CO_2 is supplied to the polymer plastic material 25 to form a fluid/polymer solution containing a sufficient amount of supercritical CO_2 for a supermicrocellular foaming process. In effect the solution can be thought of as being saturated with supercritical CO_2, which saturation process occurs over a particular saturation time period, depending on the thickness of the polymer plastic. For example, if material 25 is a sheet of soft polyvinylchloride (PVC) material, having a thickness of about 1.6 mm (1/16 inch), the time period for such operation is about 30 minutes, such time being more or less dependent on the diffusion distance of the polymer (the thickness thereof) and the diffusion characteristics of the supercritical fluid, e.g., CO_2, in the particular polymer used.

[0022] Following formation of the desired fluid/polymer material, the chamber is opened and the material is removed therefrom so that the pressure and temperature thereof rapidly assumes ambient room conditions (e.g., 25° C, 0.1 MPa (14.6 psi)). Such rapid changes in temperature/pressure conditions induce a thermodynamic instability so that foaming (cellular nucleation and cell expansion) takes place within the material. The foaming time to achieve a desired supermicrocellular foam PVC material, for example, is about one or two minutes, such time being more or less dependent on the temperature of the material prior to removal. It is found that such PVC material achieves a cell density of about 2×10^{12} cells/cc. and an average cell size of about 0.8 μm. The cell density is primarily a function of the amount of supercritical fluid in the fluid/polymer solution. A microphotograph of an exemplary cross-section of such material is shown in FIG. 6, magnified 2000 times, the cell distribution being substantially uniform throughout the material.

[0023] Similar experimental foamed materials were made using substantially the same technique. For example, a glycol modified polyethylene-terephthalate (i.e., copolyester) polymer material (PETG) was supplied with sufficient supercritical CO_2 fluid over a time period of about 10 hours and, when removed to room temperature and pressure conditions, the fluid/polymer system was found to foam in about one or two minutes, thereby producing a supermicrocellular foamed PETG material having a substantially uniform cell distribution, a cell density of about 3×10^{10} cells/cc. and an average cell size of about 5 microns. A microphotograph thereof is shown in FIG. 7 at a magnification of 1000 times.

[0024] In some cases, particularly when using a semicrystalline material, it has been found that the foaming temperature must be higher than ambient room temperature. For example, when a sheet of rigid PVC material having a thickness of 1.6 mm (1/16 inch) is used, an

effectively saturated fluid/polymer system can occur at a pressure of about 1500 psi (10.2 MPa) and a temperature of 43° C over a time period of about 15 hours. Following the formation thereof, the material is foamed at a much higher temperature than ambient room temperature, e.g., at 160° C at ambient pressure. Such foaming can be produced by removing the saturated rigid PVC polymer from the chamber 24 and placing it in a liquid glycerin bath the temperature of which is at the desired 160° C level. Supermicrocellular foaming was found to take place in about 10 seconds. In such case, an average cell size of about 1.0 micron and a cell density of about 2 X 10^{12} cells/cc. was achieved, there being a reasonably uniform distribution of such cells throughout the material. A microphotograph of such foamed rigid PVC material is shown in FIG. 8, at a magnification of 5000 times.

[0025] A similar foaming temperature 160° C was used for both low density and high density polyethylene (LDPE and HDPE) polymers. In the case of a low density sheet of PE having a thickness of 1.6 mm (1/16 inch), the formation of a suitable fluid/polymer system took place at a pressure of 20.4 mPa (3000 psi) and a temperature of 43° C over a 10 hour time period, while supermicrocellular foaming occurred at the 160° C level at ambient pressure in about 20 seconds. Such operation produced very small average cell sizes of about 0.1 micron and cell densities of about 5 X 10^{14} cells/cc. In the case of a sheet of high density PE having a thickness of 1.6 mm (1/16 inch), formation of a desired fluid/polymer system also occurred at 3000 psi and 43° C over a 10 hour time period, while foaming occurred at 160° C and ambient pressure in about 20 seconds. Such operation produced very small average cell sizes of about 0.2 microns and cell densities of about 6 X 10^{13} cells/cc. Microphotographs of exemplary foamed LDPE polymers and foamed HDPE polymers are shown in FIGS. 9 and 10, respectively, at magnifications of 5000 times (FIG. 9) and of 2000 times (FIG. 10), respectively.

[0026] In a further exemplary case, a sheet of polycarbonate polymer having a thickness of 1.6 mm (1/16 inch) was supplied with supercritical CO_2 to form a suitable fluid/polymer system at a pressure of 1500 psi (10.2 MPa) and 43° C over a 15 hour time period, while foaming occurred at 160° C and ambient pressure in about 10 seconds to produce average cell sizes of about 2 μm and cell densities of about 2 X 10^{11} cells/cc. A microphotograph of an exemplary cross-section thereof is shown in FIG. 11 at a magnification of 2000 times.

[0027] The bar diagrams depicted in FIGS. 12 and 13 show the correlation between average cell sizes and cell densities for the above discussed exemplary foamed materials. In the figures, the bars as related to each material are so designated in each case and, as can be seen, generally the smaller the cell sizes obtained the greater the cell densities that can be achieved.

[0028] While the producing of a supercritical fluid for use in the process of the invention is performed in the above particular examples at a temperature of 43° C and at pressures of 10.2 MPa (1500 psi) or 20.4 MPa (3000 psi), such temperatures can range from about 35° C to about 45° C, or higher, and such pressures can range from about 9.5 MPa (1400 psi) to about 40.8 MPa (6000 psi), or more. The supercritical fluid should have a relatively high density, e.g., for supercritical CO_2 fluid a density of about 0.016 moles per cubic centimeter to about 0.022 moles per cubic centimeter can be used.

[0029] Although the technique described above with reference to FIG. 3 is in effect a batch processing technique, foamed materials can also be made using a continuous process in which polymer plastic pellets or sheets are used. One such continuous technique uses a co-rotating twin screw extruder of a type well-known to those in the art for supplying a sheet of polymer to a chamber 38 for foaming of the polymer using a supercritical fluid.

[0030] In the embodiments mentioned above, there is a finite time which is required for a polymer material to become saturated with a supercritical fluid. i.e., for a sufficient amount of supercritical fluid to be introduced into the polymer to form a fluid/polymer system which can be appropriately foamed to provide a desired supermicrocellular foamed material. While in some cases such time can be as low as 10 minutes, e.g., when using a soft PVC material having a thickness of 0.16cm (1/16 inch), in other cases longer times may be required depending on the thickness desired. While such embodiments can be useful in many applications, in other applications it may be desirable to reduce the time need for such purpose. For example, in order to enhance the ability to use the present foaming technique to achieve relatively high production rates for obtaining supermicrocellular formed material, it is often desirable to use much shorter saturation time periods. One technique for doing so is depicted in the system shown in FIG. 18 in which a supercritical fluid is introduced into an extrusion barrel 70, for example, for injecting the saturated material into a mold.

[0031] As can be seen in the diagrammatic presentation of FIG. 18, an extrusion barrel 70 utilizes a mixing screw 71, of a type having irregular blades, as would be well known to those in the art, into which plastic pellets of a polymer material are introduced via a hopper assembly 72. The extrusion barrel is heated so that the pellets become plasticized and reach a molten state as they are moved by the mixing screw along the barrel 70. A source 82 of CO_2 gas is introduced into the extrusion barrel at a selected position along mixing screw 71 via the operation of a suitable flow control valve 73, the temperature and pressure in the extrusion barrel at that point being controlled so as to be greater than the critical temperature and pressure for converting the CO_2 in gaseous form into CO_2 in its supercritical state. The CO_2 gas may be preheated before insertion, if desired, to prevent too sudden an increase in pressure in the barrel at the higher temperature of the barrel. Alternatively, the

CO_2 gas can be converted to its supercritical state externally to the extrusion barrel and supplied to the mixing screw as a supercritical CO_2 fluid.

[0032] The supercritical CO_2 fluid is mixed with the molten polymer material by the mixing screw and such mixing enhances the subsequent diffusion into, and effective saturation of supercritical CO_2 fluid in, the polymer because the contact area of the two materials being mixed is increased by the mixing process and the depth required for diffusion is decreased thereby.

[0033] Thus, the supercritical CO_2 fluid is mixed with the molten polymer by the motion of the mixing screw. As the mixing screw rotates, it generates a two-dimensional shear field in the mixed CO_2/polymer system. The bubbles of supercritical CO_2 fluid in the polymer melt are stretched along the shear directions of the shear field. The stretched bubbles are then broken into smaller spherical shaped bubbles by the perturbation of the laminar flow which is generated by the mixing screw. The irregular blades used in the mixing screw change the orientation of the CO_2/polymer interface relative to the streamlines, which change increases the efficiency of the laminar mixing occurring therein.

[0034] The CO_2/polymer mix is supplied to a static mixer 74 which continually changes the orientation of the CO_2/polymer interface relative to the streamlines and thereby also enhances the mixing process. Static mixers for use in an extrusion barrel are well known to the art and are made and sold commercially. The diameter of static mixer 74 should be small and the static mixer can comprise a selected number of mixer elements 75, as further discussed below.

[0035] If the diameter of the static mixer elements is too large, the flow rate of the CO_2/polymer mixture therethrough is small and, consequently, the shear field generated by the static mixer elements is small. The spherical shapes of the bubbles would thereby be maintained because the surface tension would be dominant and, in effect, the surface tension would overcome the effect of the relatively small shear field. When the flow rate is too small, a static mixer is not effective for mixing the CO_2/polymer system because of such dominant surface tension. Hence, it is desirable to make the diameter of the static mixer relatively small.

[0036] The characteristic length of the static mixing which occurs in static mixer 74, i.e., the striation thickness of the mixed CO_2/polymer layers, is approximately $d/2^n$ where d is the diameter of the static mixer elements and n is the number of the mixing elements 75. Better mixing occurs when mixer elements having a small radius are used because such characteristic length of the mixing decreases as the diameter decreases, as well as when a relatively large number of mixing elements is used. The number of mixing elements and the diameters thereof can be selected so as to assure a satisfactory and adequate static mixing operation.

[0037] During the static mixing of the CO_2/polymer system, the CO_2 molecules in the bubbles also tend to diffuse somewhat into the polymer melt material which surrounds each bubble. However, the primary diffusion operation takes place in a diffusion chamber 76 into which the two-phase mixture is introduced. The mixture then becomes a complete single-phase solution in the diffusion chamber as the CO_2 diffuses into the polymer therein. The CO_2 concentration in the single-phase CO_2/polymer solution thereby produced is substantially uniform throughout the solution and the solution is effectively homogeneous. If the supercritical CO_2 fluid does not diffuse into and saturate the polymer uniformly and homogenously, the foamed structure that is ultimately formed will not be uniform because the cell morphology strongly depends on the local gas concentration in the solution.

[0038] The homogeneous and uniform fluid/polymer solution in diffusion chamber 76 is then heated in a heating section 77 thereof where the solution is rapidly heated (in a typical case the temperature may rise from about 190° C to about 245° C, for example), so as to form nucleated cells in the saturated solution due to the thermodynamic instability which is created because of the decreased solubility of the fluid/polymer solutions at the higher temperature. The greater the decrease in solubility which occurs, the higher the cell nucleation rate. To prevent the nucleated cells from growing in the extrusion barrel 30 a high barrel presssure is maintained. The solution with nucleated cells is then injected into a mold cavity 78 of a mold 79, the pressure in the mold cavity being controlled by providing a counter pressure to prevent cell growth during the mold filling process. The counter pressure is provided by the insertion of air under pressure from a source 80 thereof via shut-off valve 81. Finally, cell growth occurs inside the mold cavity when the mold cavity is expanded and the pressure therein is reduced rapidly, thereby producing a pressure instability which enhances cell growth.

[0039] Accordingly, expansion of the mold provides a molded and foamed article having the small cell sizes and high cell densities desired. By using a mixing screw for providing a shear field which produces a laminar flow of the mixed materials and then by using both a static mixer having small diameter mixing elements and a selected number of such mixing elements and a diffusion chamber, saturation of the polymer material with supercritical CO_2 fluid occurs. The time period required to provide such saturation can be reduced from that required in the embodiments of the invention discussed previously so that it is possible to achieve continuous operation at relatively high production rates that would not be possible when longer saturation times are needed.

[0040] The provison of extremely small cell sizes and high densities thereof in a foamed polymer material, as achieved when using supercritical fluids to provide the foaming operation, as described with reference to the above embodiments of the inventions brings about substantially improved properties for the foamed materials obtained, particularly compared with previous standard

cellular or microcellular foamed materials. Thus, the mechanical strengths and toughness thereof are substantially greater, even when the weight of the material (i.e., the material density) is considerably reduced. Moreover, less polymer material is used in the process and, accordingly, material is conserved and the costs thereof are reduced.

Claims

1. A method of injection molding a foamed material comprising the steps of

   providing a material to be foamed;
   plasticizing the material in a mixing screw barrel;
   introducing a foaming agent into said material to be foamed in the mixing screw barrel at a first temperature and at a first pressure at which the foaming agent is a supercritical fluid;
   in a diffusion chamber causing the mixture of material and fluid to become a complete single-phase solution;
   changing the temperature and pressure from said first temperature and said first pressure downstream of the mixing screw to a different selected second temperature and a different selected second pressure to produce a supermicrocellular foamed material containing a plurality of voids or cells distributed substantially throughout said material.

2. A method in accordance with claim 1, wherein the introduction of said supercritical fluid takes place over a time period sufficient to cause said material to become effectively saturated with said supercritical fluid.

3. A method in accordance with either of the preceding claims, the foamed material having a plurality of cells substantially uniformly distributed therein, the cell density of said cells in said material lying in a range from 10^9 to 10^{15} cells per cubic centimetre of said material, the average size of said cells being less than 2 µm, wherein the total volume of the cells formed in said foamed material comprises a fractional percentage of the total volume of said foamed material which lies within a range from 20 to 90 fraction percent.

4. A method in accordance with any one of the preceding claims, wherein the foaming agent is carbon dioxide.

5. A method according to any one of the preceding claims wherein said material to be foamed is selected from amorphous polymers, semi-crystalline polymers, liquid crystal polymers, thermoplastic polymers and elastomeric polymers.

Patentansprüche

1. Ein Verfahren zum Spritzgießen eines geschäumten Materials, umfassend die Schritte:

   Vorsehen eines zu schäumenden Materials;
   Plastifizieren des Materials in einem Mischschneckenextruder;
   Einführen eines Schäummittels in das zu schäumende Material in dem Mischschneckenextruder bei einer ersten Temperatur und bei einem ersten Druck, bei dem das Schäummittel ein überkritisches Fluid ist;
   Bewirken, dass aus dem Gemisch aus Material und Fluid in einer Diffusionskammer eine vollständige einphasige Lösung wird;
   Ändern der Temperatur und des Drucks von der ersten Temperatur und dem ersten Druck stromabwärts der Mischschnecke auf eine unterschiedliche, ausgewählte zweite Temperatur und einen unterschiedlichen, ausgewählten zweiten Druck, um ein supermikrozellulares, geschäumtes Material zu erzeugen, das eine Mehrzahl von Fehlstellen oder Zellen enthält, die im wesentlichen über das ganze Material verteilt sind.

2. Verfahren nach Anspruch 1, wobei die Einführung des überkritischen Fluids über eine Zeitspanne stattfindet, die ausreicht, um zu bewirken, dass das Material wirksam mit dem überkritischen Fluid gesättigt wird.

3. Verfahren nach einem der vorangegangenen Ansprüche, wobei das geschäumte Material eine Mehrzahl von Zellen aufweist, die im wesentlichen gleichmäßig darin verteilt sind, die Zelldichte der Zellen in dem Material in einem Bereich von 10^9 bis 10^{15} Zellen pro Kubikzentimeter des Materials liegt, die Durchschnittsgröße der Zellen geringer als 2 µm ist, wobei das Gesamtvolumen der Zellen, die in dem geschäumten Material gebildet sind, ein Prozentanteil des Gesamtvolumens des geschäumten Materials umfasst, das innerhalb eines Bereichs von 20 bis 90 Prozentanteile liegt.

4. Verfahren nach einem der vorangegangenen Ansprüche, wobei das Schäummittel Kohlendioxid ist.

5. Verfahren nach einem der vorangegangenen Ansprüche, wobei das zu schäumende Material ausgewählt ist aus amorphen Polymeren, halbkristallinen Polymeren, Flüssigkristallpolymeren, thermoplastischen Polymeren und elastomerischen Polymeren.

Revendications

1. Procédé de moulage par injection d'un matériau expansé comprenant les étapes consistant à

   fournir un matériau à expanser ;
   plastifier le matériau dans un fourreau à vis de mélange ;
   introduire un agent d'expansion dans ledit matériau à expanser dans le fourreau à vis de mélange à une première température et sous une première pression à laquelle l'agent d'expansion est un fluide supercritique ;
   dans une chambre à diffusion, transformer le mélange de matériau et de fluide en une solution à phase unique complète ;
   faire varier la température et la pression à partir de ladite première température et de ladite première pression en aval de la vis de mélange jusqu'à une seconde température choisie différente et une seconde pression choisie différente pour produire un matériau expansé supermicrocellulaire contenant un grand nombre de vides ou d'alvéoles distribués essentiellement dans tout ledit matériau.

2. Procédé selon la revendication 1, dans lequel l'introduction dudit fluide supercritique a lieu sur une période de temps suffisante pour que ledit matériau soit efficacement saturé avec ledit fluide supercritique.

3. Procédé selon l'une quelconque des revendications précédentes, un grand nombre d'alvéoles étant distribuées essentiellement uniformément dans le matériau expansé, la densité alvéolaire desdites alvéoles dans ledit matériau se situant dans la gamme allant de 10^9 à 10^{15} alvéoles par centimètre cube dudit matériau, la taille moyenne desdites alvéoles étant inférieure à 2 µm, dans lequel le volume total des alvéoles formées dans ledit matériau expansé représente une fraction en pourcentage du volume total dudit matériau expansé qui se situe dans la gamme allant de 20 à 90 %.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent d'expansion est le dioxyde de carbone.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit matériau à expanser est choisi parmi des polymères amorphes, des polymères semi-cristallins, des polymères cristallins liquides, des polymères thermoplastiques et des polymères élastomériques.

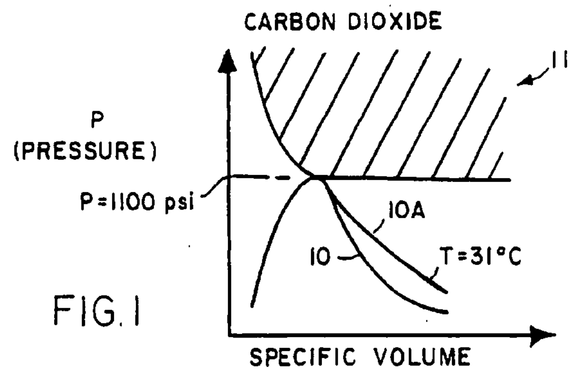


FIG. 1

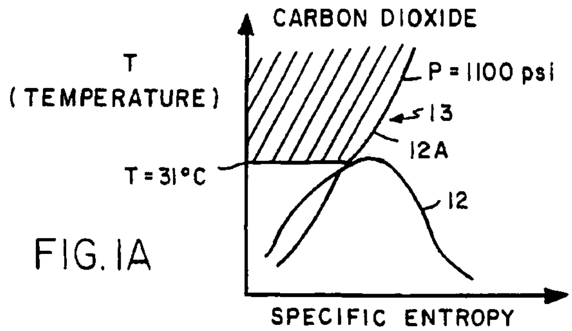


FIG. 1A

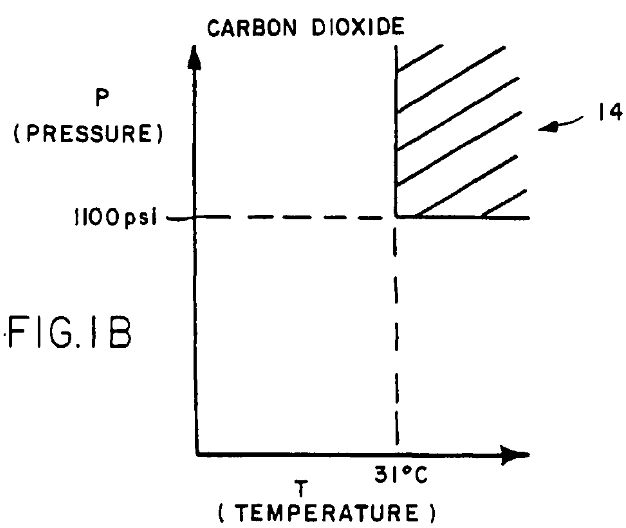


FIG. 1B

FIG. 2

SUPERCRITICAL FLUID	C.T. (°C)	C.P. (psi)
CO_2	31.1	1071.3
ETHANE	32.3	708.3
ETHYLENE	9.3	742.1
N_2	-147.0	492.3
Fr - 12	115.7	581.9
O_2	-118.6	736.2
AMMONIA	132.5	1635.7
WATER	374.2	3208.1

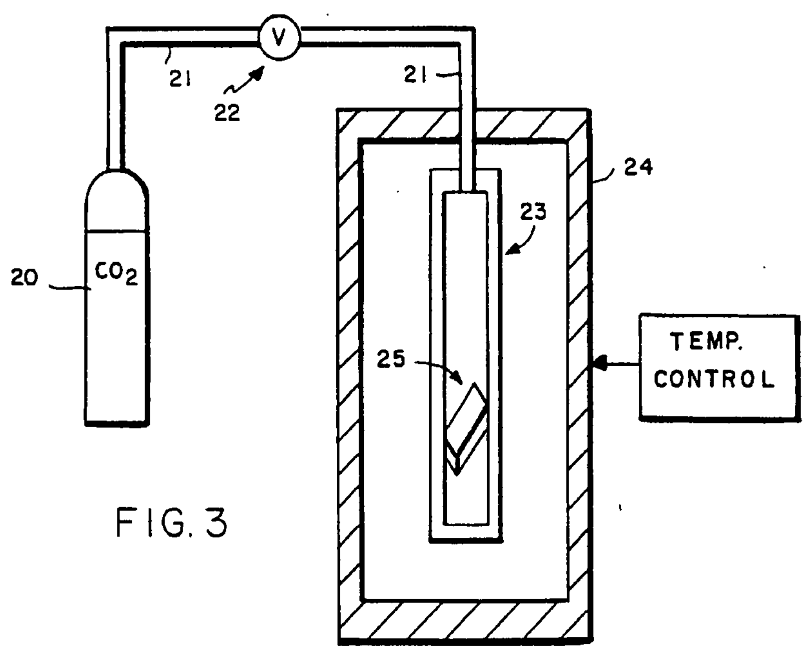


FIG. 3

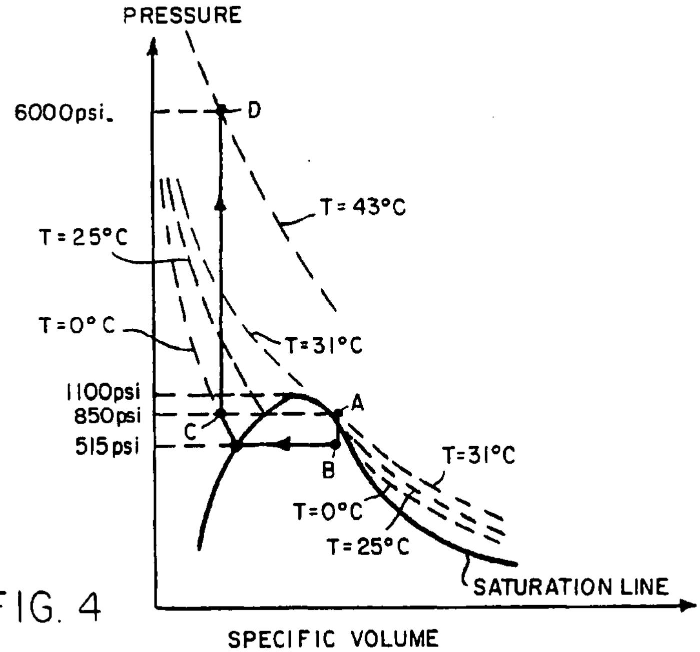

PRESSURE
6000psi
D
T = 43°C
T = 25°C
T = 0° C
T = 31°C
1100psi
850psi
515psi
A
C
B
T = 31°C
T = 0°C
T = 25°C
SATURATION LINE
SPECIFIC VOLUME

FIG. 4

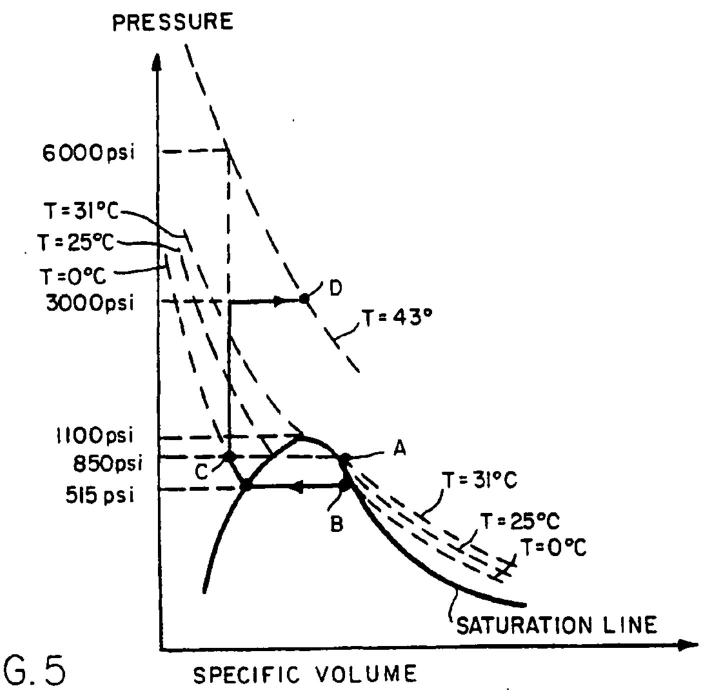
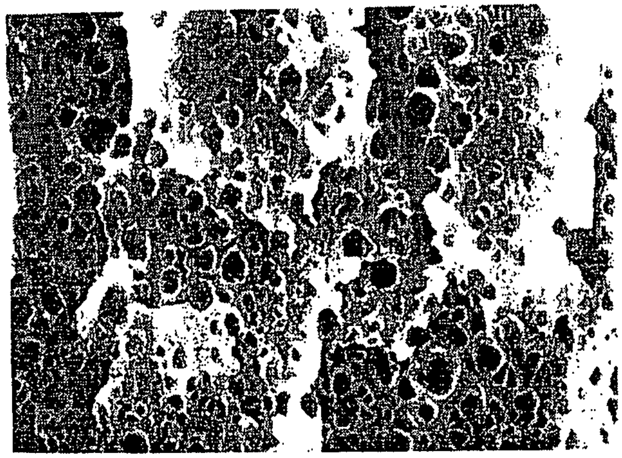
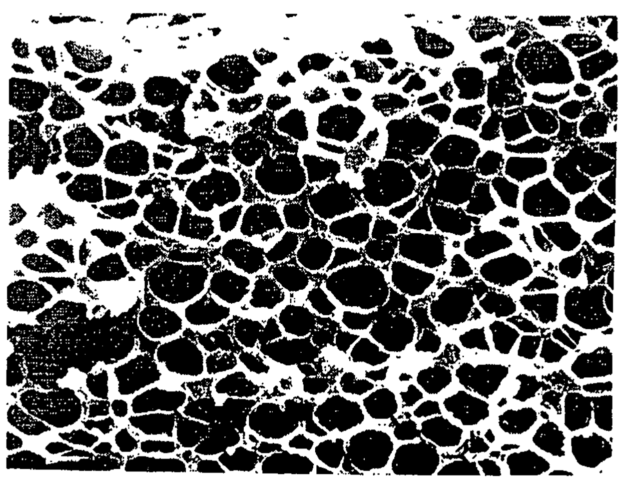

PRESSURE
6000psi
T = 31°C
T = 25°C
T = 0°C
3000psi
D
T = 43°
1100psi
850psi
515 psi
A
C
B
T = 31°C
T = 25°C
T = 0°C
SATURATION LINE
SPECIFIC VOLUME

FIG. 5



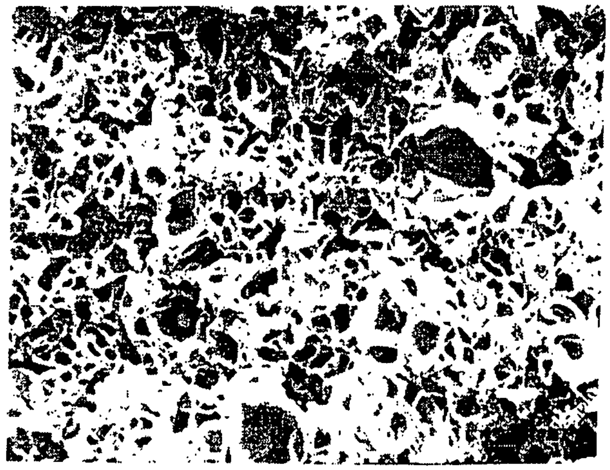
(x 2000)

FIG. 6



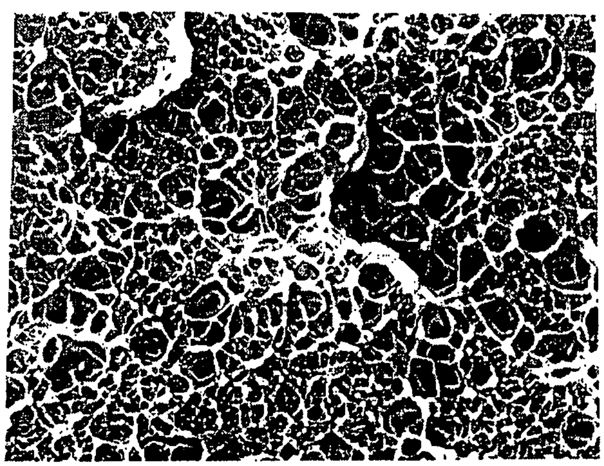
(x 1000)

FIG. 7



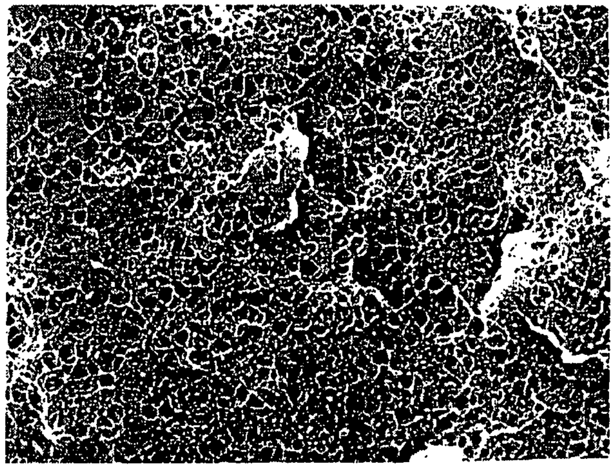
(x 5000)

FIG. 8



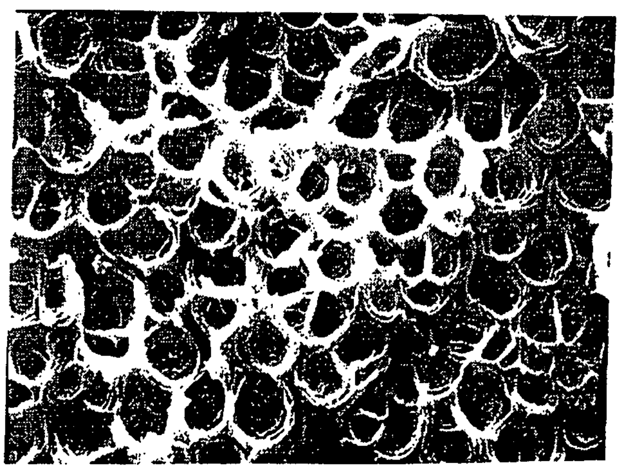
(x 5000)

FIG. 9



(x 2000)

FIG. 10



(x 2000)

FIG. 11

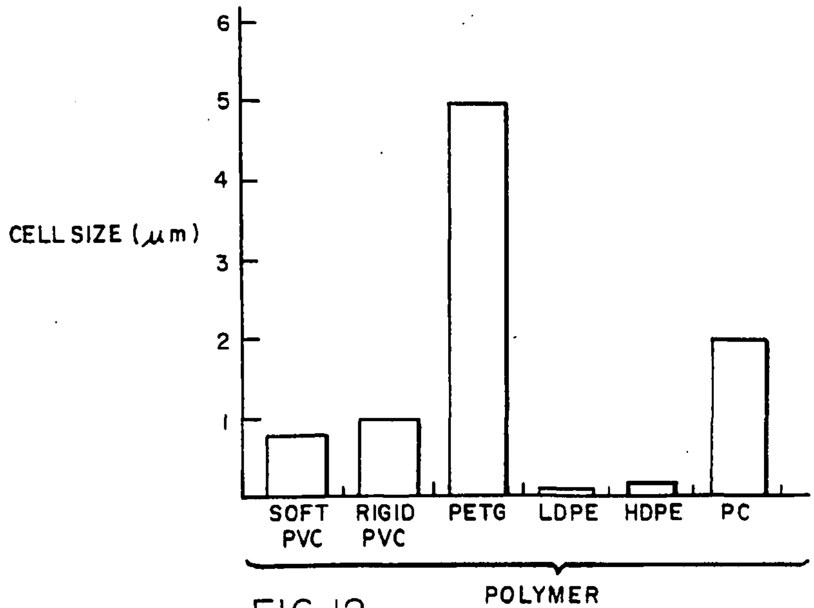

CELL SIZE (μm)
6
5
4
3
2
1
SOFT PVC
RIGID PVC
PETG
LDPE
HDPE
PC
POLYMER

FIG. 12

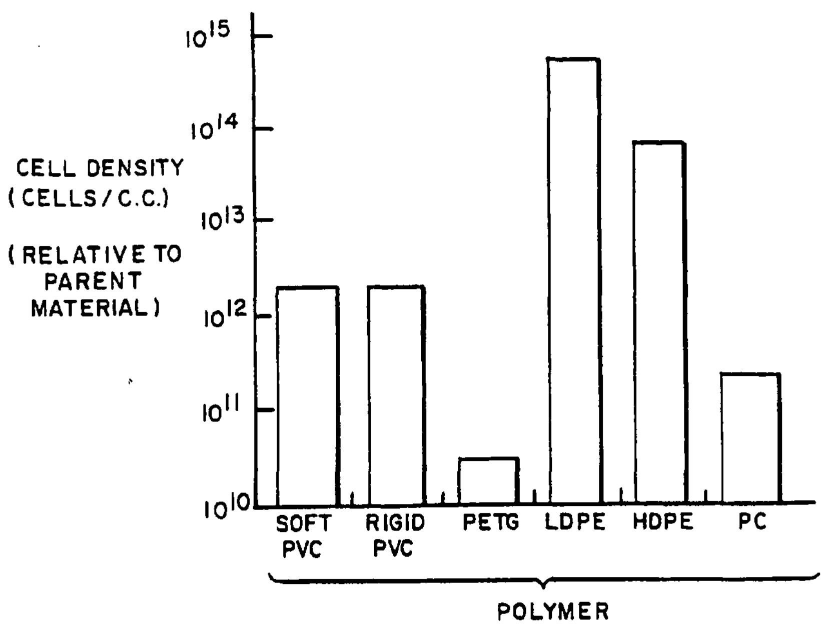

CELL DENSITY (CELLS/C.C.)
(RELATIVE TO PARENT MATERIAL)
10^15
10^14
10^13
10^12
10^11
10^10
SOFT PVC
RIGID PVC
PETG
LDPE
HDPE
PC
POLYMER

FIG. 13

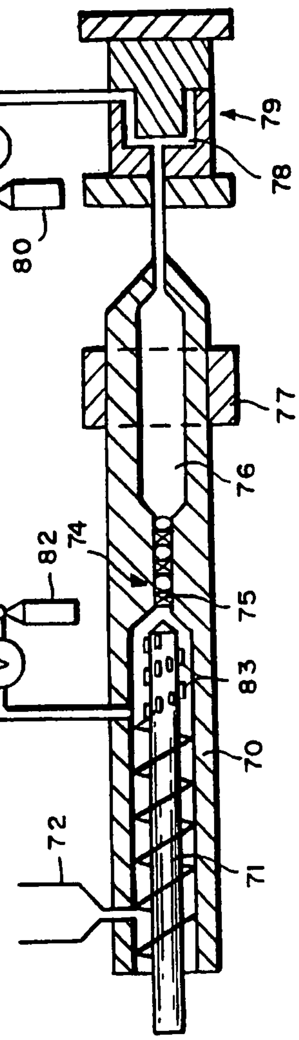


FIG.18